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TRANSMITTAL LETTER TO THE UNITED STATES				Studien 282-KGB	
DESIGNATED/ELECTED OFFICE (DO/EO/US)				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	
CONCERNING A FILING UNDER 35 U.S.C. 371				09/831566	
INTERNATIONAL APPLICATION NO. <b>PCT/EP99/08594</b>	INTERNATIONAL FILING DATE <b>9 November 1999</b>		PRIORITY DATE CLAIMED <b>13 November 1998</b>		

## TITLE OF INVENTION

**WATER-SOLUBLE NANOSTRUCTURED METAL-OXIDE COLLOIDS AND METHOD FOR PREPARING SAME**

## APPLICANT(S) FOR DO/EO/US

**Manfred T. REETZ and Michael Georg KOCH**

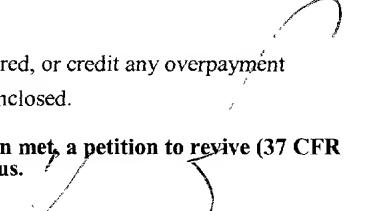
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1.  This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2.  This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3.  This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4.  A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5.  A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a.  is transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  has been transmitted by the International Bureau.
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US).
6.  A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7.  A copy of the International Search Report (PCT/ISA/210).
8.  Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a.  are transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  have been transmitted by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
9.  A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10.  An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11.  A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12.  A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 20 below concern document(s) or information included:**

13.  An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14.  An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15.  A **FIRST** preliminary amendment.
16.  A **SECOND** or **SUBSEQUENT** preliminary amendment.
17.  A substitute specification.
18.  A change of power of attorney and/or address letter.
19.  Certificate of Mailing by Express Mail
20.  Other items or information:

**Combined Declaration and Power of Attorney****Copy of PCT/EP99/08594 WO 00/29332****Form PCT/IPEA/416****Letter dated 8 January 2001****PCT Chapter II Demand****Notification of Transmittal of the International Search Report (Form PCT/ISA/220)****Copy of Receipt for Documents****Copy of PCT Request****Copy of Application (German)**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>09/831566</b>	INTERNATIONAL APPLICATION NO. PCT/EP99/08594	ATTORNEY'S DOCKET NUMBER Studien 282-KGB
21. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>		
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1,000.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00 <input checked="" type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$690.00</b>
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		□ 20    □ 30 <b>\$0.00</b>
<b>CLAIMS</b> Total claims      25 - 20 =      5 Independent claims      1 - 3 =      0 Multiple Dependent Claims (check if applicable).		<b>NUMBER FILED</b> <b>NUMBER EXTRA</b> <b>RATE</b> <b>\$90.00</b> <b>\$0.00</b> <b>\$0.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$780.00</b>
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).		<input checked="" type="checkbox"/> <b>\$390.00</b>
<b>SUBTOTAL =</b>		<b>\$390.00</b>
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		□ 20    □ 30    + <b>\$0.00</b>
<b>TOTAL NATIONAL FEE =</b>		<b>\$390.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/> <b>\$0.00</b>
<b>TOTAL FEES ENCLOSED =</b>		<b>\$0.00</b>
		<b>Amount to be: refunded</b> \$ <b>charged</b> <b>\$ 390.00</b>
<input type="checkbox"/> A check in the amount of _____ to cover the above fees is enclosed.  <input checked="" type="checkbox"/> Please charge my Deposit Account No. <b>14-1263</b> in the amount of <b>\$390.00</b> to cover the above fees. A duplicate copy of this sheet is enclosed.  <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. <b>14-1263</b> A duplicate copy of this sheet is enclosed.		
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>		
<b>SEND ALL CORRESPONDENCE TO:</b>  <b>Kurt G. Briscoe</b> <b>Norris McLaughlin &amp; Marcus</b> <b>220 East 42nd Street - 30th Floor</b> <b>New York, New York 10017</b> <b>(212) 808-0700</b>		
 <b>SIGNATURE</b> <b>Kurt G. Briscoe</b> <b>NAME</b> <b>33,141</b> <b>REGISTRATION NUMBER</b> <b>May 10, 2001</b> <b>DATE</b>		

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Date of Deposit: May 10, 2001

Studien 282-KGB  
Zi/D

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS : MANFRED T. REETZ et al  
SERIAL NO. : To be Assigned  
FILED : Herewith  
FOR : WATER-SOLUBLE NANOSTRUCTURED METAL-OXIDE  
COLLOIDS AND METHOD FOR PREPARING SAME  
ART UNIT : To Be Assigned  
EXAMINER : To Be Assigned

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May 10, 2001

Hon. Commissioner of Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

SIR:

Prior to examination, please amend the above-identified application as follows:

IN THE SPECIFICATION:

Insert the following as the new first paragraph: -- This is a 371 of PCT/EP99/08594 filed on November 9, 1999.

IN THE CLAIMS:

Cancel all of the claims in the application and substitute:

21. Additive-stabilized, water-soluble metal oxide colloids having particle sizes ranging from 0.5 - 5 nm, comprising at least one metal of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table, and stabilized by at least one water-soluble additive.
22. Colloids according to claim 21, which are monometal-oxide colloids having particle sizes ranging from 0.5 - 5 nm, comprising a metal of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table, and stabilized by at least one water-soluble additive.
23. Colloids according to claim 21, which are bimetal-oxide colloids or multimetaloxy colloids having particle sizes ranging from 0.5 - 5 nm, comprising a plurality of metals of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table, and stabilized by at least one water-soluble additive.
24. Colloids according to claim 21, which are bimetal-oxide colloids or multimetaloxy colloids having particle sizes ranging from 0.5 - 5 nm, comprising a metal of the main group of the Periodic Table and one or more metals of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table, and stabilized by at least one water-soluble additive.
25. Colloids according to claim 24, wherein said metal of the main group of the Periodic Table is tin.

26. Colloids according to claim 21, wherein said at least one water-soluble additive is selected from the group consisting of amphiphilic betains, cationic surfactants, anionic surfactants, nonionic surfactants, and water-soluble polymers.

27. A process for preparing colloids according to claim 21, said process comprising hydrolyzing or condensing at least one metal salt in an aqueous solution comprising a base in the presence of a stabilizing water-soluble additive.

28. The process according to claim 27, which is for the preparation of monometal-oxide colloids, and comprises hydrolyzing or condensing a salt of a metal of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table in an aqueous solution comprising a base in the presence of a stabilizing water-soluble additive.

29. The process according to claim 27, which is for the preparation of bimetal-oxide colloids or multi-metal oxide colloids, and comprises hydrolyzing or condensing salts of a plurality of metals of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table in an aqueous solution comprising a base in the presence of a stabilizing water-soluble additive.

30. The process according to claim 27, which is for the preparation of bimetal-oxide colloids, and comprises hydrolyzing or condensing a salt of a metal of the main group of the Periodic Table and a salt of a metal of groups VIb, VIIb, VIII, Ib or IIb of the Periodic Table in

an aqueous solution comprising a base in the presence of a stabilizing water-soluble additive.

31. The process according to claim 30, wherein said salt of said metal of the main group of the Periodic Table is  $\text{SnCl}_2$  or  $\text{SnCl}_4$ .

32. The process according to claim 27, wherein the stabilizing water-soluble additive is selected from the group consisting of amphiphilic beatins, cationic surfactants, anionic surfactants, nonionic surfacants, and water-soluble polymers.

33. The process according to claim 27, wherein the base is an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal bicarbonate, an alkaline earth metal bicarbonate, an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal phosphate, an alkaline earth metal phosphate, an alkali metal hydrogen phosphate or an alkaline earth metal hydrogen phosphate.

34. The process according to claim 33, wherein the base is  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$  or  $\text{MgCO}_3$ .

35. The process according to claim 27, which is conducted at a temperature between 20 and 100°C.

36. The process according to claim 35, which is conducted at a temperature between 50 and 90°C.

37. The process according to claim 27, which is for the preparation of bimetal-oxide colloids or multi-metal-oxide colloids, and further comprises choosing the mass ratio of metal salts to control the mass ratio of metals in the bimetal-oxide colloids or multimetal-oxide colloids.

38. A process for preparing water-soluble, nanostructured, monometal colloids, bimetal colloids or multimetal colloids each having particle sizes ranging from 0.5 - 5 nm, said process comprising:

- a) preparing monometal-oxide colloids, bimetal-oxide colloids or multimetal-oxide colloids according to the process of claim 27; and
- b) reducing said monometal-oxide colloids, bimetal-oxide colloids or multimetal-oxide colloids.

39. The process according to claim 38, which is conducted in the presence of a reduction agent selected from the group consisting of hydrogen, hypophosphite or formate.

40. A process for fixing colloids according to claim 21 onto solid supports, said

process comprising treating solid oxidic or non-oxidic solid materials with an aqueous solution of the colloids.

41. A process for fixing colloids prepared by the process according to claim 38 onto solid supports, said process comprising treating solid oxidic or non-oxidic solid materials with an aqueous solution of the colloids.

42. A process for immobilizing colloids according to claim 21, said process comprising incorporating said colloids into sol-gel-materials.

43. The process according to claim 42, wherein the sol-gel materials are prepared from gel precursors, which gel precursors are  $\text{Si}(\text{OCH}_3)_4$  or mixtures of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$  ( $n = 1$  to 4).

44. A process for immobilizing colloids prepared by the process according to claim 38, said process for immobilizing comprising incorporating said colloids into sol-gel-materials.

45. The process according to claim 44, wherein the sol-gel materials are prepared from gel precursors, which gel precursors are  $\text{Si}(\text{OCH}_3)_4$  or mixtures of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$  ( $n = 1$  to 4).

REMARKS

A new set of claims is provided which eliminates multiple dependency and otherwise makes editorial changes. Importantly, the claims have not been narrowed in any material respect. Accordingly, the claims retain the full range of equivalents.

For the Examiner's information, the new claims correspond to the previous claims as follows:

<u>New Claim</u>	<u>Previous Claim</u>
21	
22	1 + 2+ 3
23	2
24	3
25	4
26	5
27	6
28	7
29	8
30	9
31	10
32	11
33	12

MANFRED T. REETZ, ET AL  
STUDIEN 282-KGB

34	13
35,36	14
37	15
38	16
39	17
40, 41	18
42, 43	19, 20
44, 45	19, 20

Early and favorable action is earnestly solicited.

Respectfully submitted,

NORRIS MC LAUGHLIN & MARCUS, P.A.

By \_\_\_\_\_

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## **Water-soluble Nanostructured Metal-Oxide Colloids and Method for Preparing the same**

The present invention relates to mono-, bi- and multi metallic, water-soluble metal-oxide colloids, a method for preparing the same and their fixation on a support.

Nanostructured transition metal colloids are of great interest as catalysts for organic reactions, as electrocatalysts in fuel cells as well as structural elements in material science (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994). In the literature, numerous chemical and physical processes for the preparation of metal colloids are known, e. g., the chemical reduction of common metal salts, as  $\text{PdCl}_2$ ,  $\text{Pd}(\text{OAc})_2$ ,  $\text{PtCl}_4$ ,  $\text{RuCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeCl}_2$  or  $\text{AuCl}_3$ , with a wide variety of reduction agents, the photolytical, radiolytical or thermal decomposition or reduction of appropriate metal precursors, or the method of metal vaporization. Recently, electrochemical methods for the preparation of metal colloids are being used too (M.T. Reetz, S.A. Quaiser, *Angew. Chem.* **1995**, *107*, 2956; *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*, 2728). In order to prevent an undesired agglomeration of the nanoparticles into insoluble metal powders, stabilizers, such as ligands, polymers or surfactants are added in most cases (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994).

Due to ecological and economical reasons water-soluble metal colloids are of particularly great interest in industry, the synthesis of which is ideal in an aqueous medium. The aim of preparing high concentrated,

water-soluble, surfactant-stabilized metal colloids was achieved only in a few cases; however, the reduction step is relatively expensive or requires costly reduction agents, such as boron hydrides (M.T. Reetz et al., EP 0 672 765 A1, and H. Bönnemann et al., DE 4 443 705 A1).

Furthermore, bimetallic nanoparticles are often clearly superior to the nanometallic species for certain catalytic applications, for which reason the selective synthesis of bimetallic metal colloids is gaining more and more in importance (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994).

Hereby, two different metal salts are chemically or electrochemically co-reduced in organic solvents in the presence of useful stabilizers, whereby the degree of alloy formation of the particles generally depends from the difference of the reduction potentials of the two metal salts used. Therefore, not all combinations of metals are possible by this route. The use of organic solvents and/or expensive reduction agents is also unfavorable.

Due to high polarity and high surface tension of the water, it is extremely difficult, just in an aqueous medium, to produce bimetallic colloids having a high degree of alloy formation. A special challenge also consists in alloying two metals which have a significantly different reduction potential, e.g., a noble metal, such as platinum, with a distinctly less noble metal, such as ruthenium, iron, cobalt or tin, in an aqueous medium in a way as simple as possible.

Now, a surprisingly simple solution to these problems could be achieved in an approach in which the metal salts are not reduced but condensed in an aqueous medium and in the presence of a water-soluble stabilizer,

whereby the corresponding nano-structured metal oxide is formed. The stabilizer prevents the undesired formation and deposition, respectively, of insoluble metal oxide in bulk form. Working with two metal salts results in a co-condensation with formation of water-soluble colloidal bimetal oxides, whereby the size of the particles is also in the nanometer range.

The water-soluble metal-oxide colloids and bimetal-oxide colloids thus obtained can then be characterized with the aid of appropriate physical methods and can be processed to soluble or carrier-fixed catalysts. Hereby, the reduction of the colloidal metal oxide may take place with the help of reduction agents, such as hydrogen, hypophosphite or formate, without any appreciable change of the stoichiometry or of the particle size of the nanoparticles. The method allows an extension to trimetal oxides and multimetal oxides, respectively.

Contrary to the corresponding metal colloids, little is known in the literature about the preparation and the properties of metal oxide colloids of the late transitional metals. Henglein describes the preparation of colloidal  $MnO_2$  by radiolysis of  $KMnO_4$  (C. Lume-Pereira, et al., *J. Phys. Chem.* **1985**, 89, 5772), Grätzel (K. Kalyanasundaram, M. Grätzel, *Angew. Chem.* **1979**, 91, 759) as well as Harriman (P. A. Christensen, et al., *J. Chem. Soc., Faraday Trans.* **1984**, 80, 1451) obtained polymer-stabilized colloids of  $RuO_2$  from  $RuO_4$  or  $KRuO_4$ , and Thomas reported colloids of  $IrO_2$  by hydrolysis of  $H_2IrCl_6$  in the presence of a polymer (A. Harriman, et al., *New J. Chem.* **1987**, 11, 757). Furthermore, publications by Nagy can be mentioned who obtained colloidal particles of  $ReO_2$  in microemulsions by reduction of  $NaReO_4$  with hydrazine (J. B. Nagy, A. Claerbout, in *Surfactants in Solution* (K. L. Mittal, D. O. Shah, Eds.), Plenum Press, New York, **1991**, p. 363; A.

Claerbout, J. B. Nagy in *Preparation of Catalysts V* (G. Poncelet, Ed.), Elsevier, Amsterdam, **1991**, p. 705).

These colloidal oxides of noble metals must be distinguished from the publications of Matijevic, who describes metal oxides of metals, such as iron, aluminum, chromium, titanium, nickel and cerium, made by precipitation from homogenous solution (E. Matijevic, *Langmuir* **1994**, 10, 8; E. Matijevic, *Langmuir* **1986**, 2, 12), whereby the term of "colloidal" is not appropriate in this case, since the  $\mu\text{m}$  sized particles do not remain in solution in a colloidal form. Furthermore, colloidal metal oxides and metal sulfides may be mentioned, such as, for instance, CdS and CoFe<sub>2</sub>O<sub>4</sub>, which usually are prepared in microemulsions and which are used in the semiconductor technology as well as in magnetic liquids (M. P. Pilani, *Langmuir* **1997**, 13, 3266).

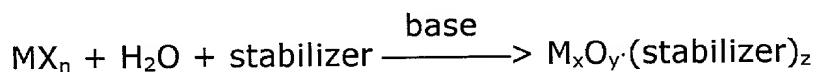
Another possibility for preparing metal oxide colloids consists in oxidizing metal colloids afterwards in a specific manner, as could be shown in the case of electrochemically prepared nanoparticles of cobalt (M. T. Reetz, et al., *Angew. Chem.* **1996**, 108, 2228; *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2092); however, this method is not possible in water as a medium. Therefore, neither this method nor other methods are suitable for making available water-soluble nanoparticles of metal or bimetal oxides in an easy way.

The new method of the controlled hydrolysis for preparing colloidal metal oxides and bimetal oxides has the following advantages:

- 1) Water as an inexpensive and ecologically benign solvent.
- 2) A nearly complete conversion of the metal precursors into soluble metal oxides or bimetal oxides (no loss of metal).

- 3) Preparation of almost monodisperse nanoparticles in a size range of 0,5-5 nm, which means a high dispersion of the metals.
- 4) Simple purification and isolation of the colloid powders by dialysis and lyophilization.
- 5) Simple reduction of the metal oxides and bimetal oxides, respectively, by using hydrogen without any significant change of the stoichiometry and the size distribution.
- 6) Complete re-dispersibility of the colloid powder in water with concentrations of up to 0.5 mole of metal per liter of water.
- 7) Handling of the metal-oxide colloids in air without any difficulties, in contrast to the corresponding colloids of noble metals which are oxidized at the surface by air.
- 8) Fixation on a solid support at the stage of the oxidized species.
- 9) Control of the stoichiometry of the bimetals within a wide range.
- 10) Numerous water-soluble surfactants and polymers can be used as stabilizers.
- 11) The process may be extended to the preparation of trimetal oxide colloids and multimetal oxide colloids.

According to the invention, the aqueous solution or, if possible, the suspension of a salt of a transition metal or a mixture of two or more metal salts is treated with the aqueous solution of a base in the presence of a water-soluble stabilizer. This results in the hydrolysis of the metal salts and the condensation and co-condensation, respectively, with formation of colloidal monometal oxides or colloidally alloyed mixed oxides.



Scheme 1. Preparation of water-soluble metal-oxide colloids ( $\text{MX}_n$  = metal salt).

In the case of preparing monometal oxides, common salts of metals of the groups VIb, VIIb, VIII, Ib and IIb of the periodic table can be used as precursors. In the case of preparing colloidal bimetal oxides (mixed oxides), two common salts of metals of the groups VIb, VIIb, VIII, Ib and/or IIb of the periodic table are used and co-condensed, respectively; the same is possible when using one of these salts in combination with the salt of a metal from the main group of the periodic table, whereby, in particular, salts of tin may be used. In the case of preparing colloidal multimetal oxides, the corresponding mixtures consisting of three or more metal salts are chosen.

Carbonates, bicarbonates, hydroxides, phosphates or hydrogen phosphates of alkali metals and alkaline earth metals, such as  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{LiHCO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $\text{CsHCO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Li}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_3\text{PO}_4$  or  $\text{K}_3\text{PO}_4$ , serve as bases. Preferred bases are  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$  or  $\text{MgCO}_3$ .

Amphiphilic betains, cationic, anionic and nonionic surfactants or water-soluble polymers are possible as stabilizers. Typical examples of the amphiphilic betains are dimethyldodecylammoniopropane sulfonate and dimethyldodecylammoniopropane carboxylate, a typical example of the cationic surfactant is  $[\text{CICH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}]^+\text{Cl}^-$ , a typical example of the anionic tenside is sodium cocoamidoethyl-N-hydroxyethyl glycinate, typical examples of the nonionic tensides are polyoxyethylenelauryl ether and polyoxyethylenesorbitanmono laurate, as well as typical examples of the water-soluble polymers are poly(vinyl

pyrrolidone) (PVP), polyethylene glycol (PEG) or alkylpoly glycoside. It is also possible to use chiral water-soluble stabilizers such as poly-L-aspartic acid, sodium salt. The hydrolysis and condensation, respectively, of the metal salts in a basic, aqueous environment, and in the presence of a stabilizer is performed in a range of temperature of from 20 °C to 100 °C, preferably between 50 °C and 90 °C. Water serves as a solvent and at the same time as a chemical reactant, whereby the concentration of the aqueous solutions of the colloidal metal oxides can amount up to 0,5 M, in relation to the metal. However, mixtures of solvents, consisting of water and water-soluble organic solvent, can also be used.

The particle size of the nanostructured metal-oxide colloids is normally between 0,5 nm and 5 nm.

In the case of preparing bimetal-oxide colloids and of multimetal-oxide colloids, the mass ratio of the metals in the product can be controlled in an easy manner by the corresponding choice of the mass ratio of the metal salts. The colloidal metal oxides thus obtained as well as their reduction products with hydrogen can be characterized by means of numerous physical methods, such as HRTEM/EDX, XRD/DFA, XPS, EXAFS and UV spectroscopy.

For preparing heterogeneous catalysts starting from water-soluble colloids of metals and of metal oxides, numerous oxidic and nonoxidic solids, for example,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{La}_2\text{O}_3$ , carbon black or activated carbon, can be used as the solid support ("Trägerung").

For that purpose, an aqueous suspension of the solid support is treated with an aqueous solution of the metal colloids or of the metal oxide colloids, which causes the nanoparticles to be deposited on the solid

support without any undesired agglomeration. It is also possible to carry out another kind of immobilization, for instance, the inclusion in sol-gel-materials by hydrolyzing  $\text{Si}(\text{OCH}_3)_4$  or mixtures of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$  ( $n = 1-4$ ) in the presence of the metal-oxide colloids. With regard to the transformation of the nanoparticles of metal oxides into the corresponding nanoparticles of metals, the various reduction agents, particularly, hydrogen, sodium hypophosphite or sodium formate, are suited for this. The reduction may be done at the stage of the colloidal solutions of the metal oxides in water, or alternatively after the fixation on the solid support and the immobilization, respectively.

The colloids of metal, bimetallics or multimetal oxides described herein can be applied as catalysts or precursors of catalysts for organic-chemical transformations, such as hydrogenations or oxidations. The application as electrocatalysts in fuel cells (e. g., Pt/Ru bimetal oxide) is also evident and of particular importance in view of the low production costs.

#### Example 1. $\text{PtRuO}_x$ (3.12-SB)

370 mg (5 mmole) of  $\text{Li}_2\text{CO}_3$  was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammoniopropane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of  $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$  and 235.9 mg (1 mmole) of  $\text{RuCl}_3 \times \text{H}_2\text{O}$  in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and of the condensation was followed by UV spectroscopy by means of the decrease of the  $\text{H}_2\text{PtCl}_6$  absorption at 260 nm. After this

band had completely disappeared, the reaction was terminated and cooled to room temperature. The colloidal solution was then filtered, in order to separate any precipitated metal oxide possibly present, and was submitted to an dialyzing process. Hereby, the colloidal metal oxide solution was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate monitored was conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 10.70 % Pt, 5.82 % Ru (this is corresponding to a molar ratio of 0,95:1)

TEM micrographs of the solution of the colloidal metal oxide solution show particles having a size distribution of  $1.5 \pm 0,4$  nm. A individual-particle-EDX- analysis of these particles indicates bimetal character, since both metals always can be detected in a molar ratio between 1:2 and 2:1.

XPS examinations of these colloids showed that ruthenium is present in the oxidation state of IV, whereas two equal parts of platinum are incorporated into the colloid in the oxidation states of II and IV, respectively.

The XRD spectrum of the sample which was reduced in a stream of H<sub>2</sub> at 120 °C shows a scatter curve, from which an average peak distance of 2.73 Å can be calculated (bulk PtRu: 2.71 Å, bulk Pt: 2.774 Å, bulk Ru: 2.677 Å). As a result, the average particle size was found to be 1.2 nm. Principally, M<sub>13</sub>-icosahedra as well as decahedra contribute to the DFA simulation of the scatter curve, whereas the proportion of larger particles of the fcc type being relatively small.

Example 2. PtRuO<sub>x</sub> (1.12-CB)

370 mg (5 mmole) of Li<sub>2</sub>CO<sub>3</sub> were weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of dimethyldodecylammonio acetate (1-12-CB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H<sub>2</sub>PtCl<sub>6</sub> × 6 H<sub>2</sub>O and 235.9 mg (1 mmole) of RuCl<sub>3</sub> × H<sub>2</sub>O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12.0 to a value of 8.5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation were observed by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. The colloidal solution was then filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of the conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely redispersible in water.

Metal content: 13.27 % Pt, 4,85 % Ru (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.4 nm

Example 3. PtRuO<sub>x</sub> (PVP)

370 mg (5 mmole) of Li<sub>2</sub>CO<sub>3</sub> as well as 3 g of poly(vinyl pyrrolidone) (PVP) were weighed in a 250 ml three-necked flask and dissolved in 80 ml of deionized water. A solution of 517.9 mg (1 mmole) of H<sub>2</sub>PtCl<sub>6</sub> × 6 H<sub>2</sub>O and 235.9 mg (1 mmole) of RuCl<sub>3</sub> × H<sub>2</sub>O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the polymer solution decreased from initially 11,5 to a value of 7.5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation was monitored by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 2.9 g of a grey colloid powder was obtained which is completely redispersible in water, MeOH, EtOH and DMF.

Metal content: 6.78 % Pt, 3.15 % Ru (this is corresponding to a molar ratio of 1.11:1)

TEM: 1.6 nm

Example 4. PtRuO<sub>x</sub> (3-12-SB), Pt/Ru = 4:1

370 mg (5 mmole) of Li<sub>2</sub>CO<sub>3</sub> was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammoniopropane sulfonate (3-12-SB) in deionized water

was added thereto. A solution of 828.6 mg (1,6 mmole) of  $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$  and 94.4 mg (0.4 mmole) of  $\text{RuCl}_3 \times \text{H}_2\text{O}$  in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for ca. 6 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the  $\text{H}_2\text{PtCl}_6$  absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 14.87 % Pt, 2,97 % Ru (this is corresponding to a molar ratio of 2,59:1)

TEM: 1.5 nm

Example 5.  $\text{PtRuO}_x$  (3-12-SB), Pt/Ru = 1:4

370 mg (5 mmole) of  $\text{Li}_2\text{CO}_3$  was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammoniopropane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 207.2 mg (0.4 mmole) of  $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$  and 377.4 mg (1.6 mmole) of  $\text{RuCl}_3 \times \text{H}_2\text{O}$  in 20 ml of deionized water was added dropwise thereto at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially

11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for 6 hours, whereby the progress of the hydrolysis and the condensation was monitored by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 9.67 % Pt, 11.27 % Ru (this is corresponding to a molar ratio of 1:2.26)

TEM: 1.5 nm

#### Example 6. PtO<sub>2</sub> (3-12-SB)

296 mg (4 mmole) of Li<sub>2</sub>CO<sub>3</sub> and 674 mg (2 mmole) of PtCl<sub>4</sub> were weighed in a 250 ml three-necked flask and dissolved in 160 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammonio-propane sulfonate (3-12-SB) in deionized water was added thereto. The solution was stirred at 80 °C for 24 hours, whereby a discoloration from yellow orange to red brown occurred. After termination of the reaction, the colloidal platinum dioxide solution was filtered, and, subsequently, the solution was dialyzed twice against 1.5 l of deionized water in a Nadir dialyzing tube. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.3 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 22.41 % Pt

TEM: 1.7 nm

Example 7. PtRuO<sub>x</sub>-colloid having a chiral tenside as stabilizer

370 mg (5 mmole) of Li<sub>2</sub>CO<sub>3</sub> was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of 3-(N,N-dimethyldodecylammonio-2-(S)-hydroxy butyrate (3-12-CB\*) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H<sub>2</sub>PtCl<sub>6</sub> x 6 H<sub>2</sub>O and 235.9 mg (1 mmole) of RuCl<sub>3</sub> x H<sub>2</sub>O in 20 ml of deionized water was added thereto dropwise with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for 26 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.24 % Pt, 3.92 % Ru (this is corresponding to a molar ratio of 0.82:1)

TEM: 1.6 nm

Example 8. PtRuO<sub>x</sub>-colloid having a chiral polymer as stabilizer

37 mg (0.5 mmole) of Li<sub>2</sub>CO<sub>3</sub> as well as 500 mg of poly-L-aspartic acid, sodium salt were weighed in a 50 ml two-necked flask and dissolved in 10 ml of deionized water. A solution of 51.8 mg (0.1 mmole) of H<sub>2</sub>PtCl<sub>6</sub> × 6 H<sub>2</sub>O and of 23.6 mg (0.1 mole) of RuCl<sub>3</sub> × H<sub>2</sub>O in 5 ml of deionized water was added dropwise thereto with strong stirring over a period of 10 minutes at room temperature. Hereby, the pH value of the polymer solution decreased from initially 11,5 to a value of 7.5 after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for 26 hours. The progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 500 mg of a grey colloid powder was obtained which is completely re-dispersible in water, MeOH, EtOH and DMF.

Metal content: 3.78 % Pt, 1.98 % Ru (this is corresponding to a molar ratio of 0.98:1)

TEM: 1.6 nm

Example 9. PtSnO<sub>x</sub> (3-12-SB)

74 mg (1 mmole) of Li<sub>2</sub>CO<sub>3</sub> as well as 103.6 mg (0.2 mmole) of H<sub>2</sub>PtCl<sub>6</sub> × 6 H<sub>2</sub>O were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecylammonio-

propane sulfonate (3-12-SB) in deionized water. A solution of 37.8 mg (0.2 mmole) of  $\text{SnCl}_2 \times 2\text{H}_2\text{O}$  in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the  $\text{H}_2\text{PtCl}_6$  absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0,6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.79 % Pt, 2.67 % Sn (this is corresponding to a molar ratio of 1.55:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

#### Example 10. $\text{PtFeO}_x$ (3-12-SB)

74 mg (1 mmole) of  $\text{Li}_2\text{CO}_3$  as well as 103.6 mg (0.2 mmole) of  $\text{H}_2\text{PtCl}_6 \times 6\text{H}_2\text{O}$  were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecyl-ammoniopropane sulfonate (3-12-SB) in deionized water. A solution of 39.8 mg (0.2 mmole) of  $\text{FeCl}_2 \times 4\text{H}_2\text{O}$  in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the

decrease of the  $\text{H}_2\text{PtCl}_6$  absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0,6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.12 % Pt, 1.24 % Fe (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

Example 11.  $\text{PtWO}_x$  (3-12-SB)

74 mg (1 mmole) of  $\text{Li}_2\text{CO}_3$  as well as 103.6 mg (0.2 mmole) of  $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$  were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecyl-ammoniopropane sulfonate (3-12-SB) in deionized water. A solution of 66.0 mg (0.2 mmole) of  $\text{Na}_2\text{WO}_4$  in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the  $\text{H}_2\text{PtCl}_6$  absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide present and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically.

Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 4.61 % Pt, 0.78 % W (this is corresponding to a molar ratio of 5.5:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

Example 12. PtRuWO<sub>x</sub> (3.12-SB)

370 mg (5 mmole) of Li<sub>2</sub>CO<sub>3</sub> was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of dimethyldodecylammoniopropane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H<sub>2</sub>PtCl<sub>6</sub> × 6 H<sub>2</sub>O and 141.5 mg (0.6 mmole) of RuCl<sub>3</sub> × H<sub>2</sub>O and of 66.0 mg (0.2 mmole) of Na<sub>2</sub>WO<sub>4</sub> in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 3 hours. Hereby, the pH value of the tenside solution decreased from initially 11.4 to a value of 9.8, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 22 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H<sub>2</sub>PtCl<sub>6</sub> absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.8 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 8.31 % Pt, 2.91 % Ru, 0.73 % W

TEM: 1.5 nm

Example 13: Reduction of the colloidal metal oxide solution

1 g of the isolated and purified PtRuO<sub>x</sub> (3-12-SB) colloid prepared in accordance to example 1 was dissolved in 100 ml of deionized water in a Schlenck vessel under protective gas. After an ultrasonic treatment for 30 min, the Schlenck vessel was subjected to a slight evacuation for a short while, a gas balloon filled with hydrogen was connected therewith, and the solution was then stirred in a H<sub>2</sub> atmosphere at room temperature for 24 hours. The initially dark green to brown solution changes its color to deep black during this time. The colloidal solution can be lyophilized or can directly be processed on a carrier material for fixation.

TEM micrographs of the colloidal solution of PtRu show particles having a size distribution of 1,7±0,4 nm. A EDX individual particle analysis of these particles indicates an almost complete formation of an alloy.

XPS examinations with these colloids showed that both platinum and ruthenium are present in a metallic form.

Example 14: Fixation of a PtRu colloid on Vulcan as the solid support

3.552 g Vulcan XC-72R of the Cabot Company was weighed in a 1 l three-necked flask and suspended in 200 ml of a buffer solution (Citrate buffer, 50 mM, pH 4.7). 300 ml of an aqueous solution of PtRu(3-12-SB) (888 mg of noble metal) prepared according to specification of example 13 was added dropwise thereto under a protective gas at 50 °C for 3 hours. Subsequently, the suspension was stirred at 50 °C for 40 hours and stirred for another 16 hours at 100 °C. After cooling, the black suspension was centrifuged, the supernatant solution was decanted, the

catalyst was washed twice with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 8.00 % Pt, 4.62 % Ru

Particle sizes: colloid without carrier: 2.2±0.6 nm

colloid with carrier: 2.3±0.6 nm

HRTEM micrographs of the catalyst show a homogenous distribution of the PtRu nanoparticles on the solid support.

Example 15: Fixation of a PtRuO<sub>x</sub> colloid on Vulcan as the solid support

3.552 g Vulcan XC-72R of the Cabot Company which previously was surface oxidized with a solution of NaOCl was weighed in a 1 l three-necked flask and suspended in 200 ml of water. Then, 300 ml of an aqueous solution of PtRuO<sub>x</sub> (3-12-SB) (888 mg of noble metal) prepared according to specification of example 1 was added dropwise thereto at 60 °C for 3 hours. Then, 0,1 M HCl was added dropwise there, until the solution reached a pH value of 2.5, and the suspension was stirred at 50 °C for 40 hours. After cooling, the black suspension was centrifuged, the supernatant solution was decanted, the catalyst was washed twice with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 14.32 % Pt, 8.45 % Ru

Example 16: Fixation of a PtRuO<sub>x</sub> colloid on activated carbon as the solid support

5.7 g of activated carbon was weighed into a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRuO<sub>x</sub> (3-12-SB) (300 mg of noble metal) which was prepared according to specification of example 1 was dropped thereto within 1 hour at 50 °C. Subsequently, the solution was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the supernatant clear

solution was decanted, the catalyst was washed three times with 200 ml methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.72 % Pt, 1.26 % Ru

Example 17: Fixation of a PtRu colloid on alumina as the solid support

5.7 g of Al<sub>2</sub>O<sub>3</sub> was weighed in a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRu (3-12-SB) (300 mg of noble metal) prepared according to specification of example 13 was added dropwise thereto under a protective gas at 50 °C within 1 hour . Subsequently, the suspension was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the catalyst was filtered, washed three times with 200 ml methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.91 % Pt, 1.70 % Ru

Example 18: Fixation of a PtRuO<sub>x</sub> colloid on La<sub>2</sub>O<sub>3</sub> as the solid support

5.7 g of La<sub>2</sub>O<sub>3</sub> was weighed in a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRuO<sub>x</sub> (3-12-SB) (300 mg of noble metal) prepared according to specification of example 1 was added dropwise thereto at 50 °C within 1 hour. Subsequently, the suspension was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the catalyst was filtered, washed three times with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.83 % Pt, 1.88 % Ru

Example 19: Immobilization of a PtRuO<sub>x</sub> colloid in sol-gel-materials

1.2 ml (8 mmole) of tetramethoxy silane (TMOS) was initially added to a 2 ml polypropylene vessel, and 0,5 ml of an aqueous solution of a PtRuO<sub>x</sub> (3-12-SB) colloid (10 mg of noble metal; 20 g/l), prepared accor-

ding to the specification of example 1, and 50 µl of a 0,1 M solution of NaF was pipetted thereto. Subsequently, the vessel was sealed and agitated on a Vortex mixer at room temperature for 10 seconds. After a heating up has become evident, the black mixture was allowed to stand, whereupon a gelation of the solution occurred ca. 10 seconds later. Now, the gel was submitted to an ageing process in a sealed vessel at room temperature, for 24 hours and then dried at 37 °C in a drying oven for 3 days. To wash out the stabilizer, the gel was refluxed in 30 ml of ethanol for 3 days, centrifuged and washed again with 30 ml of ethanol, centrifuged again and finally dried in a drying oven at 37 °C for 4 days. 630 mg of a grey powder is obtained.

Metal content: 0.92 % Pt, 0.56 % Ru

Example 20: Hydrogenation of cinnamic ethyl ester

250 mg of a PtRuO<sub>x</sub>/activated carbon (10 mg of noble metal) catalyst, prepared according to example 16, was weighed in a glass reactor which is equipped with a high speed stirrer. The reactor was sealed, connected to a thermostat and tempered to 25 °C. Following repeated processes of evacuation and argonization of the reactor, 60 ml of absolute methanol was added thereto, and the vessel was repeatedly evacuated for a short time at an agitator power of 2000 rpm. After stirring for 60 min in an atmosphere of H<sub>2</sub>, 2 ml of cinnamic ethyl ester was injected, and the initial activity of the hydrogenation was determined by means of the time-dependant change of the H<sub>2</sub>-level of the buret.

Activity: 150 ml of H<sub>2</sub>/(g of noble metal·min). Under the same conditions, the classical Adams-catalyst showed a lower activity: 38 ml of H<sub>2</sub>/(g of noble metal·min).

C l a i m s

1. Water-soluble monometal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from metals of the groups VIb, VIIb, VIII, Ib or IIb of the periodic table, which are stabilized by water-soluble additives.
2. Water-soluble bi- and multimetal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from metals of the groups VIb, VIIb, VIII, Ib, IIb of the periodic table, which are stabilized by water-soluble additives.
3. Water-soluble bi- and multimetal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from a metal of the main group and from one or more metals of the groups VIb, VIIb, VIII, Ib, IIb of the periodic table, which are stabilized by water-soluble additives.
4. Colloids according to claim 3, wherein the metal of the main group of the periodic table is tin.
5. Colloids according to claims 1 - 4, wherein amphiphilic betains, cationic, anionic and nonionic surfactants or water-soluble polymers are used as water-soluble additives.
6. A process for producing additive-stabilized, water-soluble, mono-, bi- and multi metallic metal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, characterized in that metal salts or mixtures of two or more metal salts are hydrolyzed or condensed

or co-condensed, respectively, in basic aqueous solutions in the presence of a stabilizer in form of the additive.

7. The process according to claim 6, characterized in that salts of metals of the groups VIb, VIIb, VIII, Ib or IIb of the periodic table are hydrolyzed or condensed, respectively, in order to prepare water-soluble, monometallic metal-oxide colloids.
8. The process according to claim 6, characterized in that mixtures of two or more salts of metals of the groups VIb, VIIb, VIII, Ib and/or IIb of the periodic table are hydrolyzed or co-condensed, respectively, in order to prepare water-soluble, bi- or multi metallic metal-oxide colloids (mixed metal-oxide colloids).
9. The process according to claim 6, characterized in that mixtures of a salt of a metal of the groups VIb, VIIb, VIII, Ib or IIb and of a salt of a metal of a main group of the periodic table are hydrolyzed or co-condensed, respectively, in order to prepare water-soluble, bimetallic metal-oxide colloids.
10. The process according to claim 9, wherein the salt of a metal of a main group of the periodic table is  $\text{SnCl}_2$  or  $\text{SnCl}_4$ .
11. The process according to claims 6 - 10, wherein water-soluble amphiphilic betains, cationic, anionic or nonionic surfactants or water-soluble polymers are used as stabilizer in form of an additive.

12. The process according to claims 6 - 11, wherein a carbonate, bicarbonate, a hydroxide, a phosphate or a hydrogen phosphate of an alkali metal or an alkaline earth metal is used as a base.
13. The process according to claim 12, wherein  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$  or  $\text{MgCO}_3$  are used as a base.
14. The process according to claims 6 - 13, characterized in that the reaction temperature is between 20 and 100 °C, preferably, between 50 and 90 °C.
15. The process according to claims 6 and 8 to 14, characterized in that the mass ratio of the metals in the bi- or multi metallic metal-oxide colloids is controlled by the corresponding choice of the mass ratio of the metal salts.
16. The process for preparing water-soluble, nanostructured, mono-, bi- and multi metallic metal colloids having particle sizes of 0,5 nm to 5 nm, characterized in that the corresponding metal-oxide colloids can be produced according to the claims 6 to 15 and subsequently be reduced.
17. The process according to claim 16, wherein hydrogen, hypophosphite or formate are used as a reduction agent.
18. The process for fixation of the metal-oxide colloids prepared according to the claims 1 to 5, and of the metal-oxide colloids which are prepared therefrom according to the claims 16 to 17 on solid supports, characterized in that solid oxidic or non oxidic solid materials are treated with aqueous solutions of the colloids.

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19. The process for immobilization of the metal-oxide colloids which are prepared according to the claims 1 to 5, and of the metal-oxide colloids which are prepared therefrom according to the claims 16 to 17, characterized in that they are incorporated in sol-gel-materials.
  20. The process according to claim 19, wherein sol-gel-materials are used, for which  $\text{Si}(\text{OCH}_3)_4$  or mixtures of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$  ( $n = 1$  to 4) are used as gel precursors.

Abstract

The present invention relates to water-soluble, mono-, di- and multi-metallic metal-oxide colloids as well as to a method for preparing the same and to their fixation on a solid support. This method is characterized in that the targeted synthesis of soluble metal-oxide colloids is achieved by the controlled hydrolysis of a noble metal precursor in the presence of a water-soluble stabilizer. The metal-oxide colloids can be reduced according to the needs into corresponding metal colloids. The fixation of the nanoparticles on the solid support can be carried out both at the oxidized or reduced state of said nanoparticles.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought  
on the invention entitled

on the invention entitled

Water-Soluble Nanostructured Metal-Oxide Colloids and Method for  
the specification of which is attached hereto,                   Preparing Same  
or was filed on

as Application Serial No.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 52 547.8. Germany 11/13/1998  
(Number) (Country) (Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/EP99/08594	11/09/1999	pending
(Application Serial No.)	(Filing Date)	(Status)
(patented, pending, abandoned)		

(Application Serial No.) (Filing Date) (Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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